

SYMPOSIUM ON GEOCHEMISTRY AND CHEMISTRY OF OIL SHALE
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MAJOR AND TRACE ELEMENTS IN MAHOGANY ZONE OIL SHALE IN TWO CORES
FROM THE GREEN RIVER FORMATION, PICEANCE BASIN, COLORADO

By

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LONG ABSTRACT

The Parachute Creek Member of the lacustrine Green River Formation contains thick sequences of rich oil-shale. The richest sequence and the richest oil-shale bed occurring in the member are called the Mahogany zone and the Mahogany bed, respectively, and were deposited in ancient Lake Uinta. The name "Mahogany" is derived from the red-brown color imparted to the rock by its rich-kerogen content.

Geochemical abundance and distribution of eight major and 18 trace elements were determined in the Mahogany zone sampled from two cores, U. S. Geological Survey core hole CR-2 and U. S. Bureau of Mines core hole O1-A (Figure 1). The oil shale from core hole CR-2 was deposited nearer the margin of Lake Uinta than oil shale from core hole O1-A. The major- and trace-element chemistry of the Mahogany zone from each of these two cores is compared using elemental abundances and Q-mode factor modeling.

The results of chemical analyses of 44 CR-2 Mahogany samples and 76 O1-A Mahogany samples are summarized in Figure 2. The average geochemical abundances for shale (1) and black shale (2) are also plotted on Figure 2 for comparison. The elemental abundances in the samples from the two cores are similar for the majority of elements. Differences at the 95% probability level are higher concentrations of Ca, Cu, La, Ni, Sc and Zr in the samples from core hole CR-2 compared to samples from core hole O1-A and higher concentrations of As and Sr in samples from core hole O1-A compared to samples from core hole CR-2. These differences presumably reflect slight differences in depositional conditions or source material at the two sites.

The Mahogany oil shale from the two cores has lower concentrations of most trace metals and higher concentrations of carbonate-related elements (Ca, Mg, Sr and Na) compared to the average shale and black shale. During deposition of the Mahogany oil shale, large quantities of carbonates were precipitated resulting in the enrichment of carbonate-related elements and dilution of most trace elements as pointed out in several previous studies.

Q-mode factor modeling is a statistical method used to group samples on the basis of compositional similarities. Factor end-member samples are chosen by the model. All other sample compositions are represented by varying proportions of the factor end-members and grouped as to their highest proportion. The compositional similarities defined by the Q-mode model are helpful in understanding processes controlling multi-element distributions. The models for each core are essentially identical. A four-factor model explains 70% of the variance in the CR-2 data and 64% of the O1-A data (the average correlation coefficients are 0.84 and 0.80, respectively). Increasing the number of factors above 4 results in the addition of unique instead of common factors. Table I groups the elements based on high factor-loading scores (the amount of influence each element has in defining the model factors). Similar elemental associations are found in both cores. Elemental abundances are plotted as a function of core depth using a five-point weighted moving average of the original data to smooth the curve (Figure 3 and 4). The plots are grouped according to the four factors defined by the Q-mode models and show similar distributions for elements within the same factor.

Factor 1 samples are rich in most trace metals. High oil yield and the presence of illite characterize the end-member samples for this factor (3, 4) suggesting that adsorption of metals onto clay particles or organic matter is controlling the distribution of the metals. Precipitation of some metals as sulfides is possible (5).

Factor 2 samples are high in elements commonly associated with minerals of detrital or volcanogenic origin. Altered tuff beds and lenses are prevalent within the Mahogany zone. The CR-2 end-member samples for this factor contain analcime (3) which is an alteration product within the tuff beds of the Green River Formation. Those from O1-A contain much less analcime, but do contain dawsonite (4). The presence of dawsonite in the samples from core hole O1-A may be

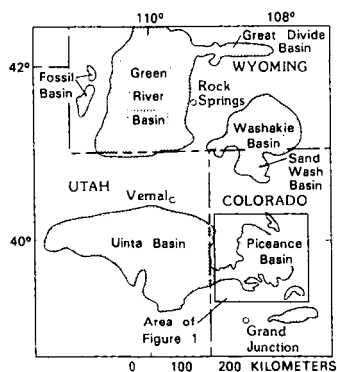
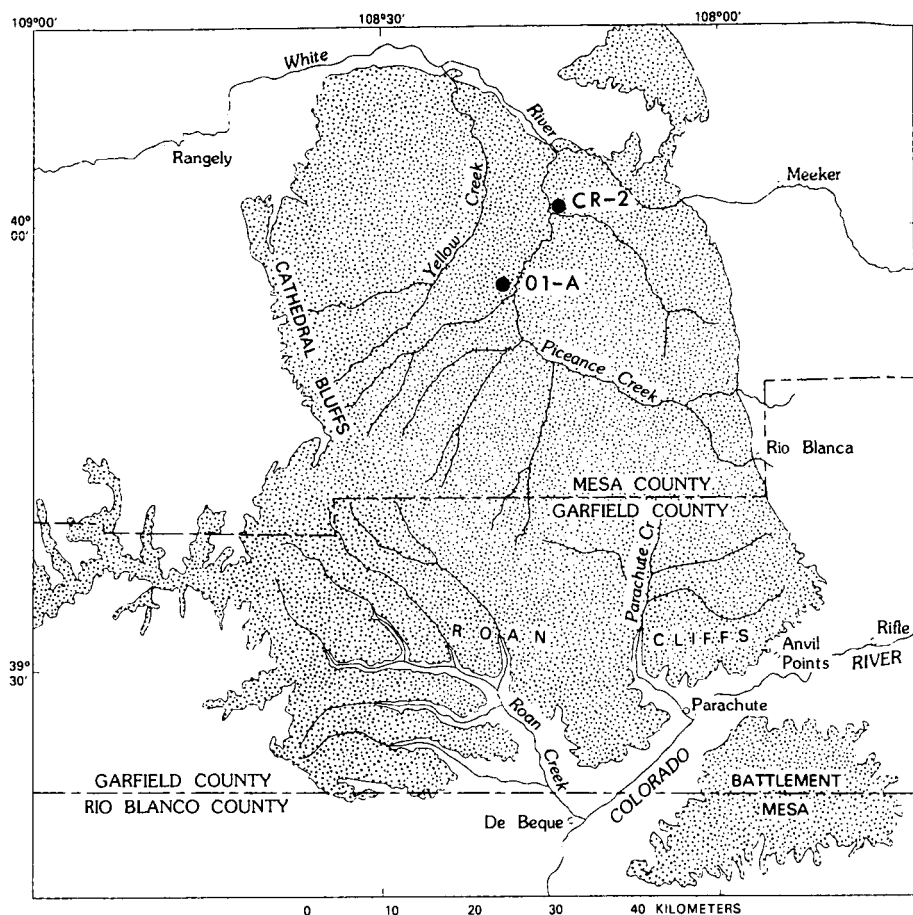


Figure 1. Index map of Piceance basin showing location of core holes CR-2 and O1-A.

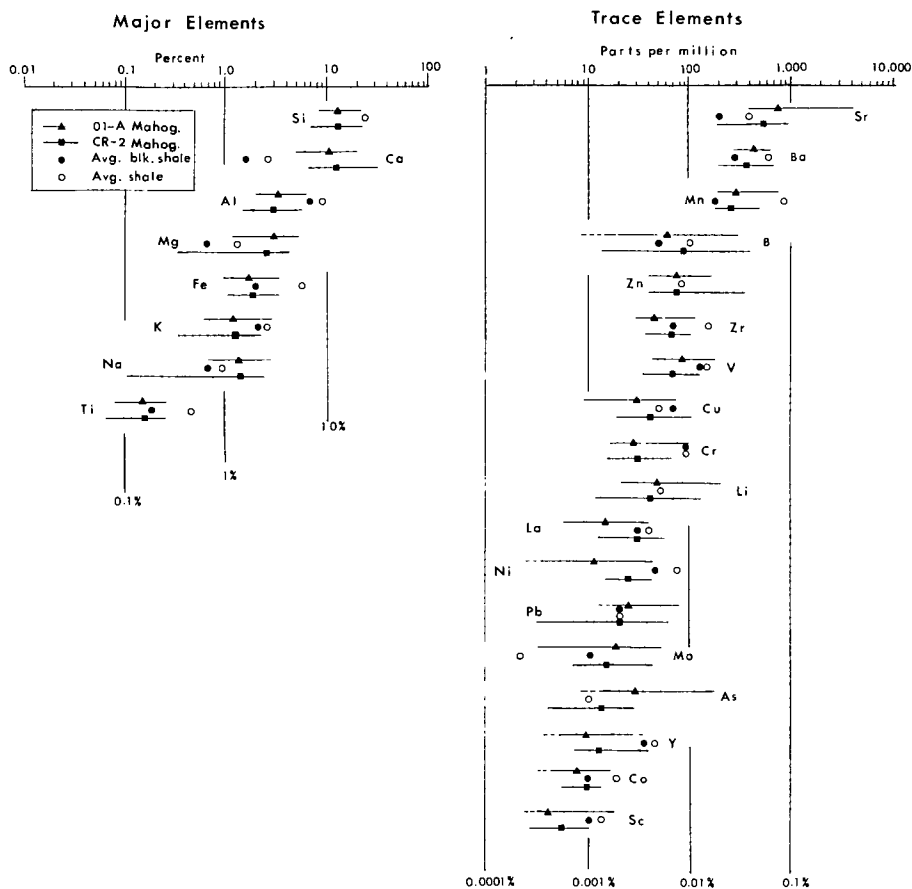


Figure 2. Observed ranges and geometric means for O1-A and CR-2 Mahogany zone core samples. Average shale (3) and average black shale (4) are also represented.

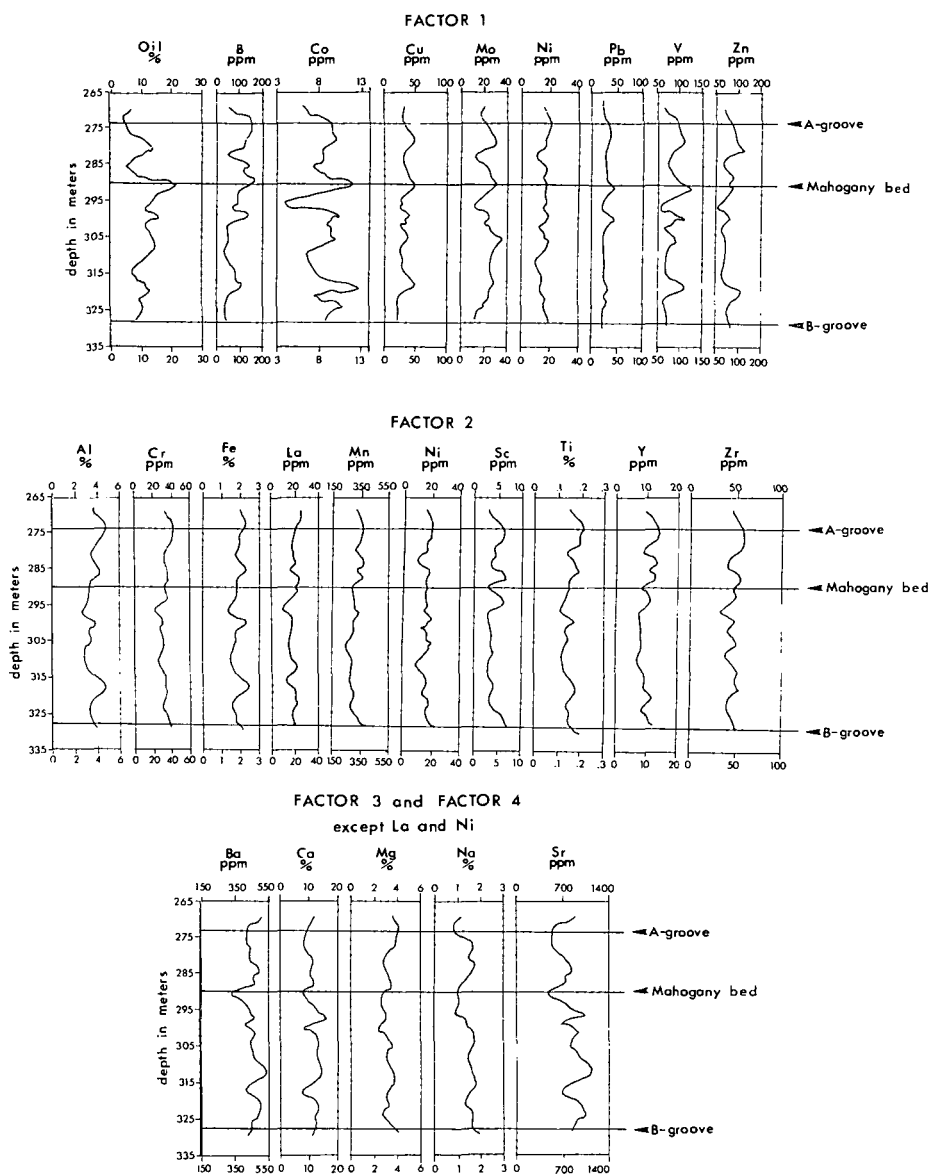


Figure 3. Distribution of elements in core O1-A as a function of core depth. Elements are grouped into the Q-mode model factors. Elements designated as excepted are plotted in a previous factor.

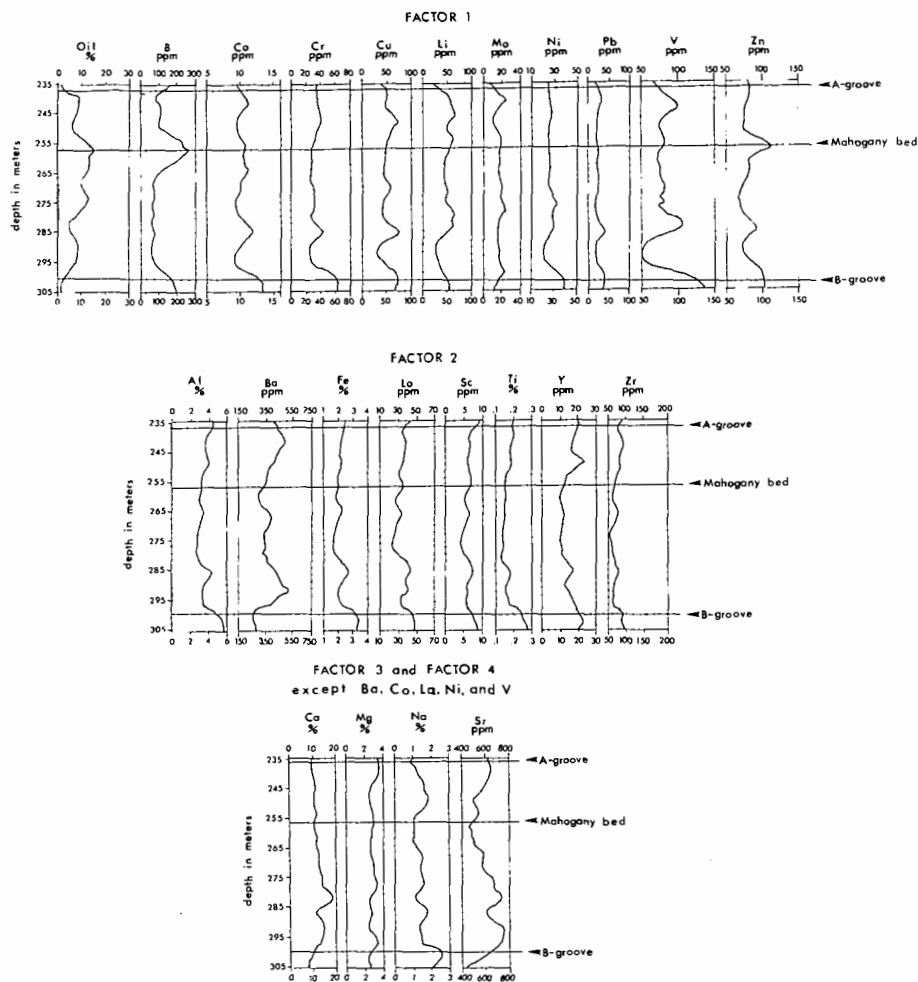


Figure 4. Distribution of elements in core CR-2 as a function of core depth. Elements are grouped into the Q-mode model factors. Elements designated as excepted are plotted in a previous factor.

due to the reaction of analcime with CO_2 . The reaction consumes analcime and produces quartz and dawsonite (6).

Factor 3 and Factor 4 samples are similar in the sense that both are carbonate-type samples. The samples contain both dolomite and calcite (3, 4). Barium, Sr and La are enriched in Factor 3 samples. Lanthanum substitutes diadochically for Ca in carbonates (7); Ba and Sr probably precipitated as carbonates. Factor 4 samples contain Co, Ni and V. The importance of these metals in defining the carbonate-rich factor is not obvious. All three metals are known to form organometallic compounds (7) which may account for their concentration in these samples.

TABLE I
COMPOSITIONAL VARIABLES IN O1-A AND CR-2 MAHOGANY OIL SHALE
AS TO THEIR Q-MODE MODEL FACTOR

Factor 1		Factor 2		Factor 3		Factor 4	
O1-A	CR-2	O1-A	CR-2	O1-A	CR-2	O1-A	CR-2
B	B	Al	Al	Ba	Ba	Ca	Ca
Co	Co	Cr	Ba	Ca	Ca	Mg	Co
Cu	Cu	Fe	Fe	La	Mg	Na	La
Mo	Cr	La	K	Mg	Na	Ni	Ni
Ni	Li	Mn	La	Na	Sr	Sr	Sr
Pb	Mo	Ni	Sc	Sr			V
Zn	Ni	Sc	Ti				
V	Pb	Ti	Y				
	V	Y	Zr				
		Zr					

LITERATURE CITED

- (1) Krauskopf, K. B., Introduction to Geochemistry, New York, McGraw-Hill Book Co., p. 617 (1979).
- (2) Vine, J. D. and Tourtelot, E. B., Geochemistry of Black Shale Deposits--A Summary Report, Economic Geology, v 65, pp. 253-272 (1970).
- (3) Dean, W. E., Pitman, J. K. and Harrach, G. H., Geochemical and Mineralogical analyses of U. S. Geologic Survey Oil-Shale Core CR-2, Piceance Creek Basin, Colorado, U. S. Geological Survey Open-file Report 81-596, pp. 1-25j (1981).
- (4) Robb, W. E., Dept. of Energy, unpublished data.
- (5) Saether, O. M., Runnells, D. D. and Meglen, R. R., Trace Elements in Rich Oil Shales of the Mahogany Zone Concentrated by Differential Density Centrifugation, in Trace elements in oil shale progress report, U. S. Dept. of Energy Report COO-10298-1, p. 237-255 (1980).
- (6) Brobst, D. A. and Tucker, J. D., X-Ray Mineralogy of the Parachute Creek Member, Green River Formation, in the Northern Piceance Creek Basin, Colorado, U. S. Geological Survey Professional Paper 803, p. 53 (1973).
- (7) Rankama, Kalervo and Sahama, Th. G., Geochemistry, Chicago, The University of Chicago Press, p. 912 (1950).